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Effect of sol aging time on the anti-reflective properties of silica coatings templated with phosphoric acid

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ABSTRACT

Silica anti-reflective coatings have been prepared by a sol–gel dip-coating process using the sol containing phosphoric acid as a pore-forming template. The effect of the aging time of the sol on the anti-reflective properties has been investigated. The surface topography of the silica AR coatings has been characterized. With increasing sol aging time, more over-sized pores larger than 100 nm are formed in the silica coatings. These could act as scattering centers, scattering visible light and thereby lowering transmittance. The optimal aging time was identified as 1 day, and the corresponding silica coatings showed a maximum transmittance of 99.2%, representing an 8% increase compared to the bare glass substrate.

Introduction

Anti-reflective (AR) coatings that can increase light transmission have been widely used in various fields, such as glass laser applications, solar collectors, cathode-ray tubes, and so on [1–3]. Hence, the development of high-performance and cost-effective AR coatings is highly desired. Sol–gel-derived silica AR coatings have been extensively studied owing to their advantages of low cost, simple operation, controllable microstructure, and good optical properties. To enhance transmittance, the basic requirement is to vary the refractive index of the AR coating. The addition of a removable templating agent to form pores is an effective method. For sol–gel-derived silica AR coatings, most of the pore-forming templates are organic agents, such as F127 [4] and CTAB [5]. Recently, we have designed a novel route to develop AR coatings by using inorganic agents, such as H_3PO_4, as pore-forming templates [6]. In that work, we prepared AR coatings by a spin-coating process, demonstrated the feasibility of using H_3PO_4 as a template, and examined the effect of H_3PO_4 concentration on transmittance [6]. Compared to the spin-coating process, the dip-coating process is more promising due to its advantage in large-area and preparative-scale deposition. In this study, we have used the dip-coating process to deposit AR silica coatings onto glass substrates, and have investigated the effect of the aging time of the sol on transmittance.

Experimental procedure

Sample preparation

Chemicals, namely tetraethyl orthosilicate (TEOS), deionized water, hydrochloric acid (HCl, 36–38%), phosphoric acid (H_3PO_4, 85%), and absolute ethanol (EtOH), were used without further purification.

1. Silica sol was prepared by a sol–gel process. TEOS, deionized water, and hydrochloric acid were mixed in a molar ratio of 1:3:0.004 (TEOS:H_2O:HCl). The mixture was stirred in an ice-water bath until it became transparent and homogeneous.
2. H_3PO_4 was diluted with EtOH in a molar ratio of 1:66 (H_3PO_4:EtOH) and stirred for 10 min. The H_3PO_4 diluted with EtOH was then added to the silica sol obtained in the Step 1 in a molar ratio of 4:6 (H_3PO_4:TEOS), and the mixture was stirred for 1 h in an ice-water bath.
3. In order to study the effect of sol aging time, the sol was aged at 0 °C for 1 day, 7 days, and 17 days, respectively.
4. Silica coatings were deposited on both sides of thoroughly cleaned glass slides as substrates (thickness: 1.0 mm, size: $25 \times 75\ mm^2$) through a dip-coating process by means of a dip coater (SYDC-300, Shanghai SAN-YAN Technology Co. Ltd.,

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China). For this, the glass slide substrate was immersed in the solution and then pulled up at a constant withdrawal speed of 2000 μm s^{-1}.

5. The coated samples were heated to 400 °C at a rate of 1 °C min^{-1} and kept at this temperature for 2 h in a programmable muffle furnace. Thereafter, the samples were immersed in boiling water for 40 min and then dried at 200 °C for 2 h.

Sample characterization

Transmittance spectra of the samples with silica AR coatings were measured on a visible spectrophotometer (723PC, Shanghai Precision Instrument Co. Ltd., China) at room temperature. The surface topography of the silica AR coatings was analyzed using a field-emission scanning electron microscope (FE-SEM) (JSM-7800F Prime, JEOL Ltd., Japan).

Results and discussion

The microstructure of sol–gel coatings is related to hydrolysis and condensation of silicon alkoxides, which can be catalyzed by acid or base during the sol–gel process. Under conditions of acid catalysis, the growth of clusters consisting of siloxane with hydroxyl groups tends to be in the form of linearly or randomly branched chains. Consequently, the clusters are cross-linked, forming sols with a certain level of viscosity. Silica coatings derived from sols formed under acid catalysis tend to be dense and the pore volume is extremely low [7]. In this study, to obtain high porosity, H_3PO_4 was added to the sol as a pore-forming template.

AR silica coatings were deposited on glass substrates by a sol–gel dip-coating process using sols containing H_3PO_4 as a pore-forming template, and this was followed by immersion in boiling water to remove the H_3PO_4 template. The relationship between the aging time of the sol containing H_3PO_4 as a template and the transmittance of the final coated samples was investigated. Fig. 1 shows transmittance spectra of the coated samples prepared from sols with different aging times. The transmittance spectrum of the bare glass substrate without a coating is also shown in Fig. 1 for comparison. All of the samples with silica AR coatings showed maximum transmittances above 95.5%, while the bare glass substrate showed a maximum transmittance of about 91.2%. Clearly, the transmittances of all of the coated samples were higher than that of the bare glass substrate. Note that the aging time of the sol appears to have a significant effect on the transmittances of the coated samples. It is observed that the peak transmittance decreases with increasing aging time of the sol. In addition, the optimal aging time of the sol was identified as 1 day, and the highest peak transmittance for samples coated on both sides reached up to 99.2%, representing an 8% increase compared to the bare glass substrate.

The transmission intensity is attenuated by scattering effects. It is required that the pore size is substantially smaller than the wavelength of the light, and the pore distribution must be homogeneous in order not to cause scattering [3]. The scattering intensity depends on the ratio of the scattering center size to the wavelength of light, and the smaller the ratio, the most transmitting is the medium [8]. The FE-SEM images in Fig. 2 show the surface morphologies of the coated samples prepared from sols aged

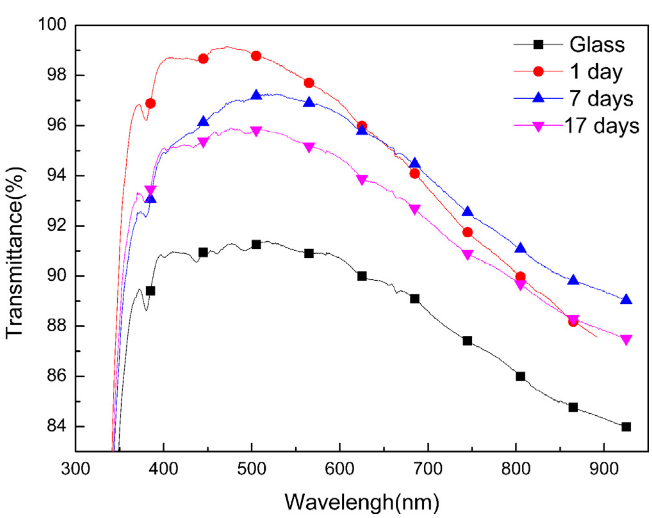

Fig. 1. Transmittances of coated samples prepared using sols aged for different times, along with that of the bare glass substrate.

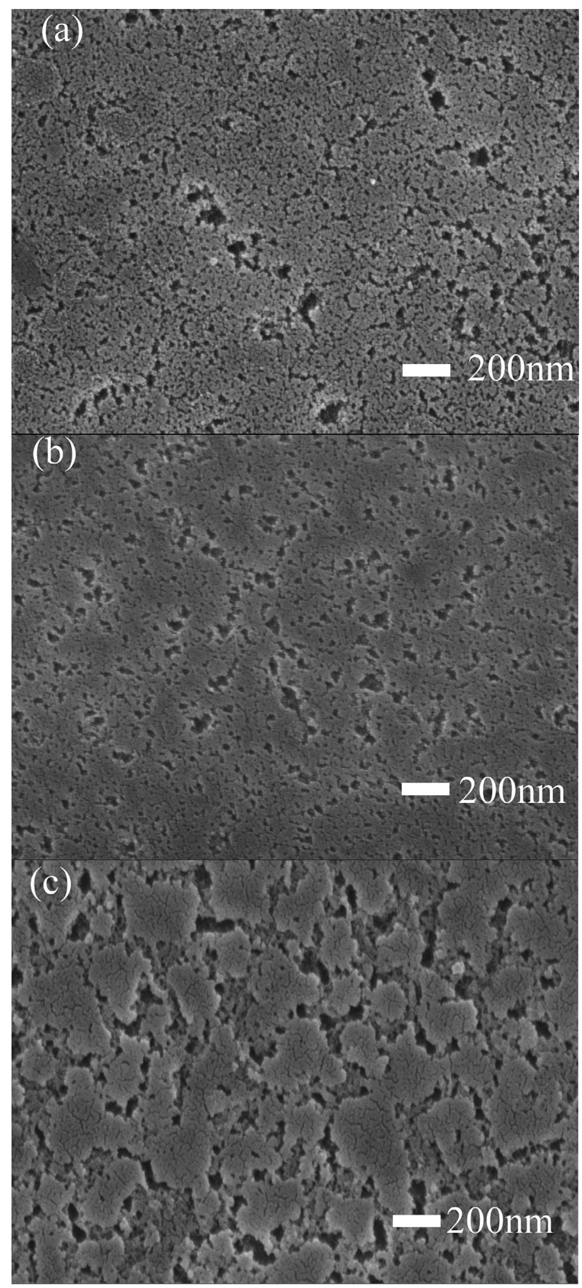

Fig. 2. FE-SEM images of coated samples prepared using sols aged for different times.

for 1, 7, and 17 days, respectively. Many tiny pores of size ca. 10–20 nm appeared in the surface of the coatings, confirming that H_3PO_4 serves as a pore-forming agent, as we have reported previously [6,9]. It can also be seen that there were few over-sized pores larger than 100 nm in Fig. 2a, whereas the numbers of such over-sized pores increased with prolonged aging time of the sol in Fig. 2b,c. It is deduced that, during aging of the sol, the silica clusters keep growing by cross-linking. More H_3PO_4 molecules as the pore-forming template tend to aggregate. Finally, after H_3PO_4 is removed by immersion in hot water, the over-sized pores larger than 100 nm are formed in the silica coatings, and they are distributed heterogeneously. Incidentally, when the sols used in this study were aged beyond 30 days, they became gels and could not be used for coating. The difference in spectral transmission behavior for the coated samples with different aging times of the sols, as shown in Fig. 1, is caused mostly by variation in the number of over-sized pores within the silica coatings. Such over-sized pores larger than 100 nm are of the same order as the wavelength of visible light. They could thus act as scattering centers [3,10], thereby weakening the anti-reflective ability of the coatings, resulting in reduced transmittance.

Conclusion

Silica AR coatings on glass substrates have been prepared by a sol–gel dip-coating process using the sol containing H_3PO_4 as a template, and have been demonstrated to show excellent anti-reflective performance. It has been found that the aging time of the sol has a significant effect on the transmittance of the coated glass. With increasing sol aging time, more over-sized pores larger than 100 nm are formed in the silica coatings. These could act as scattering centers, scattering visible light and thereby lowering transmittance. The best performance, with a maximum peak transmittance of up to 99.2%, was obtained when the aging time of the sol was 1 day.

Acknowledgements

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